Supplementary Information

for

Development of Low-Temperature SnO_2-Au Gas Sensors for H_2S Detection in Food Freshness Monitoring

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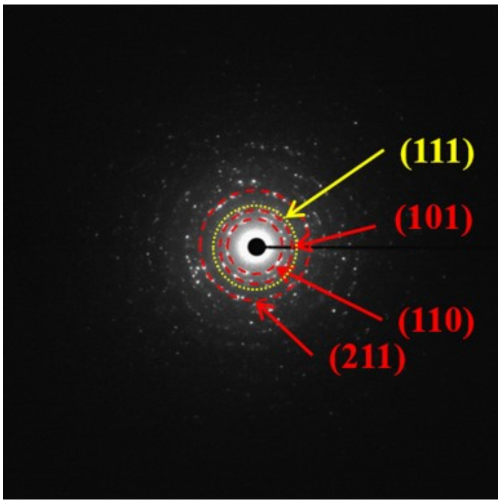
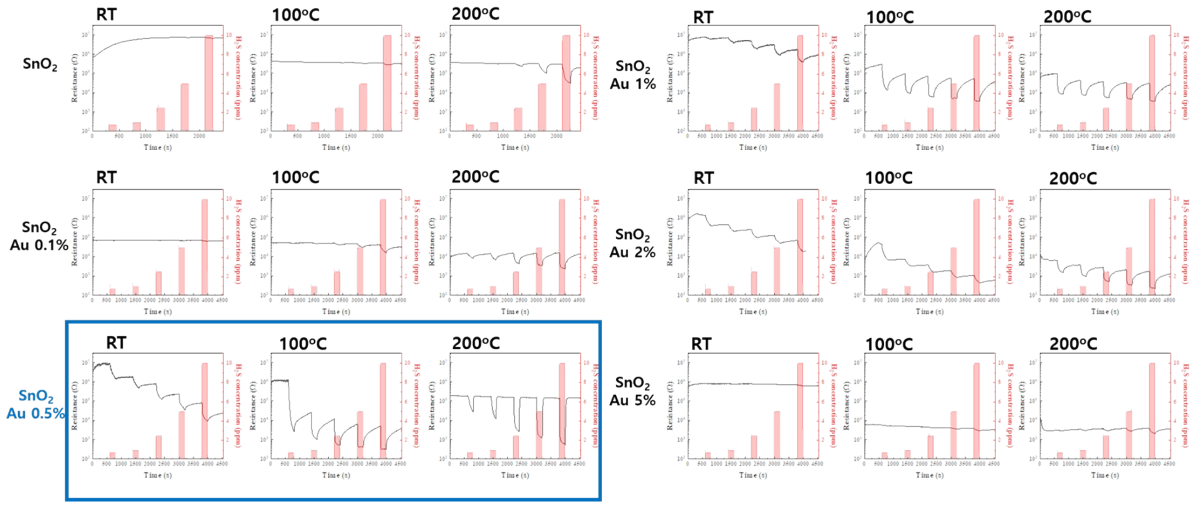
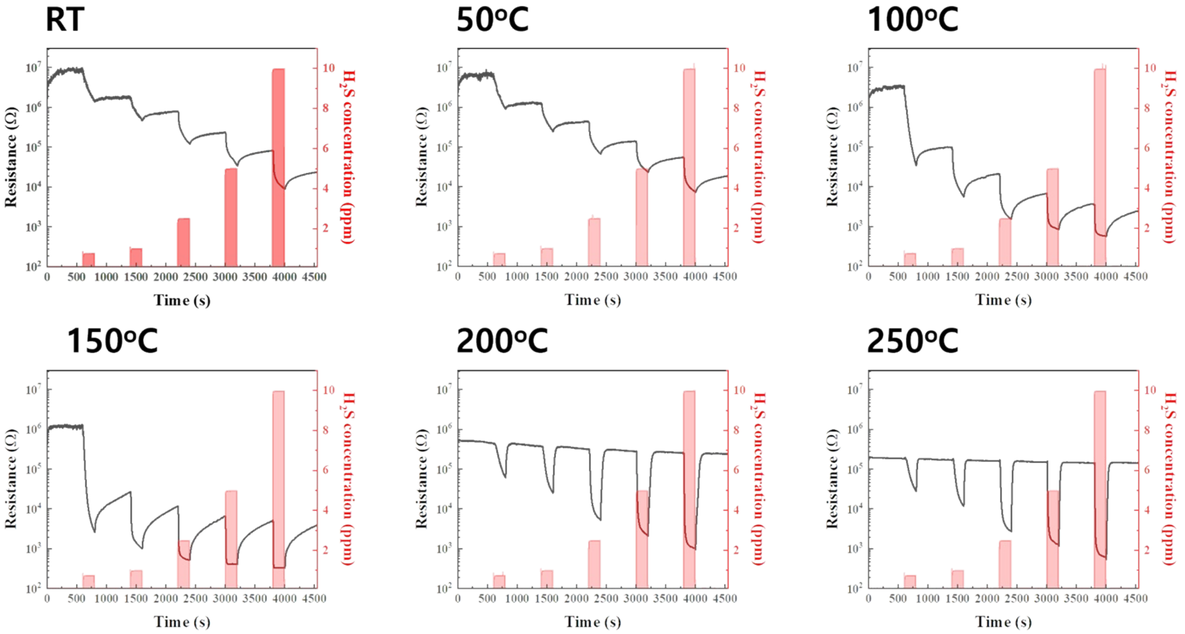
* None of the material has been published or is under consideration elsewhere, including the Internet.



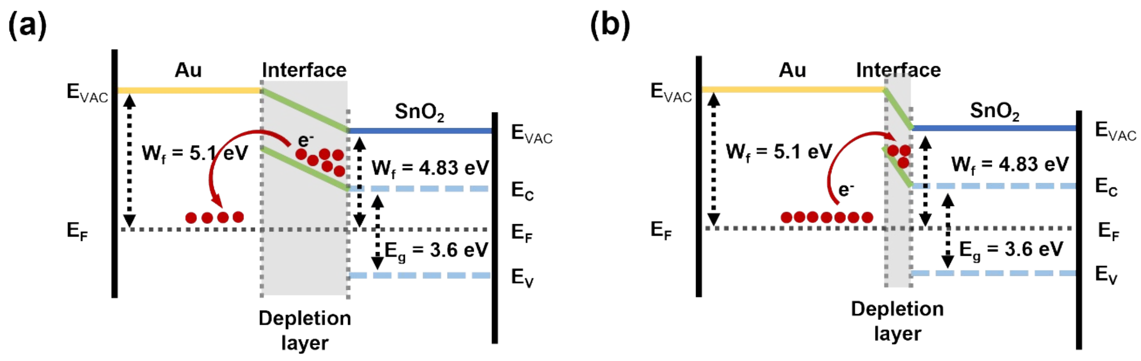
Supplementary Figure 1. SAED analysis result of the SnO_2-Au 0.5 wt% hollow nanofiber. Ring patterns are observed, indicating (101), (110), and (211) planes for the SnO_2 and a (111) plane for Au.



Supplementary Figure 2. Gas sensing characteristics of SnO_2-Au hollow nanostructures with different Au contents ratios of 0 ,0.1, 0.5, 1, 2, and 5 wt% to H_2S gas in the range from 500 ppb to 10 ppm at different operating temperature from room temperature to 200^{o}C.



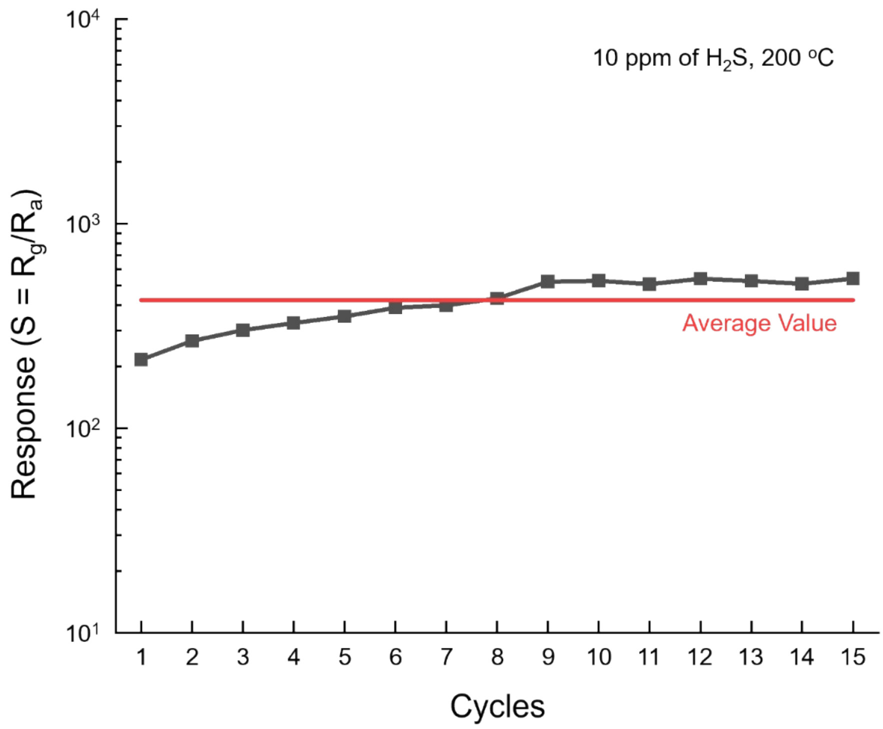
Supplementary Figure 3. Detailed gas sensing characteristics of SnO_2-Au 0.5wt% gas sensor to H_2S gas in the range from 500 ppb to 10 ppm with different operating temperature from room temperature to 250°C.



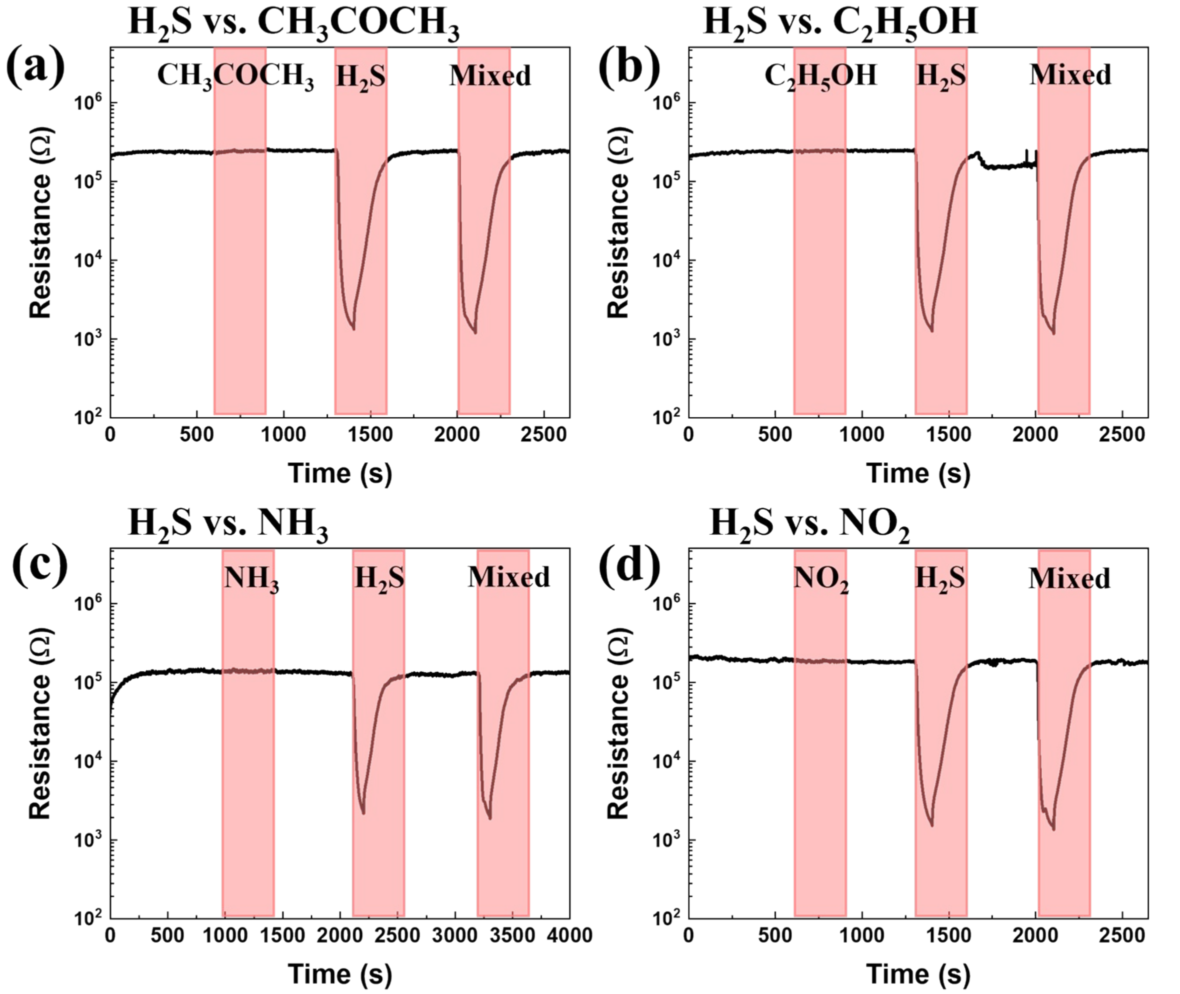
Supplementary Figure 4. Band diagram of the SnO_2-Au 0.5 wt% gas sensor at 200°C in (a) air and (b) H_2S environment.

The enhancement of gas sensing performance after adding 0.5wt% Au to SnO_2 can be attributed to two main mechanisms: electronic sensitization and chemical sensitization.[1] During the electronic sensitization process, carrier transfer occurs between the Au nanoparticles and SnO_2 due to the mismatch in work functions, leading to the formation of potential barriers. As illustrated in **Supplementary Figure 4(a)**, because Au has a higher work function, electrons generated during the sensing process migrate from the conduction band of SnO_2 into the Au until the Fermi levels equalize.[2-4] This transfer results in the formation of a Schottky barrier and an increase in the thickness of the electron depletion layer, which can suppress the recombination of separated electron-hole pairs and induce a significant change in resistance when exposed to target gases, thereby leading to a much higher response. Meanwhile, during the chemical sensitization process, the Au could facilitate the dissociation of oxygen molecules to produce more reactive chemisorbed oxygen ions which then spill over the surface of SnO_2 to react with more target gas molecules.[5-7] Thus, the chemical sensitization is also known as the spillover effect. As exhibited in **Supplementary Figure 4(b)**, oxygen molecules will preferentially adsorb on the Au metal nanoparticles and then be dissociated into O^- which then spill over to the surface of SnO_2. Taking the reducing gas as an example, the large amount of

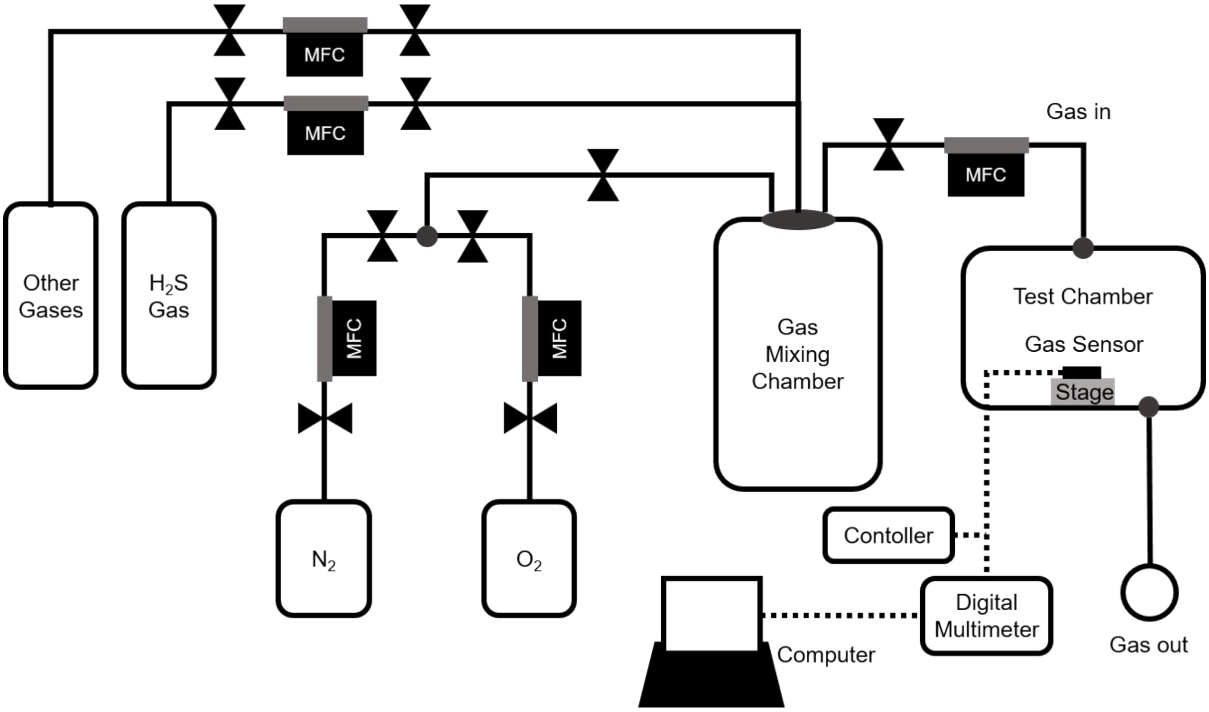
O^- could react with more target (reducing) gas molecules and cause the release of electrons, resulting in the rapid resistance change and thus the significant improvement of the gas sensing performance.



Supplementary Figure 5. Sensitivity stability over 15 cycles of H_2S measurement tests at 10 ppm H_2S and 200°C using the SnO_2-Au 0.5 wt% gas sensor.



Supplementary Figure 6. Mixed gas sensing performance of the SnO_2-Au 0.5 wt% gas sensor by fixing the H_2S (10 ppm) gas with each gas as CH_3COCH_3 (50 ppm), C_2H_5OH (50 ppm), NH_3 (200 ppm), and NO_2 (20 ppm).



Supplementary Figure 7. Schematic of the gas sensing systems.

Materials	**H_2S Concentration (ppm)**	**Operation Temperature (°C)**	**Response (R_a/R_g)**	**References**
Pt-SnO_2 hollow spheres	1	250	10.8	[8]
ZnO-SnO_2 nanospheres	10	300	99.6	[9]
Ag doped-SnO_2 films	450	100	1.38	[10]
Au/SnO-SnO_2 nanosheets	100	240	82.27% ((R_g-R_a)/R_a))	[11]
SnO_2-NiO nanostructures	20	60	250	[12]
SnO_2-Au hollow nanostructures	10	200	270.231	**This work**

Table 1. Performance comparison data of the SnO_2-based H_2S gas sensors.

References

[1] L. Zhu, et al., "Advances in Noble Metal-Decorated Metal Oxide Nanomaterials for Chemiresistive Gas Sensors: Overview", Nano-Micro Letters, 15, 89, 2023.

[2] J. Lee, et al., "High-performance gas sensor array for indoor air quality monitoring: the role of Au nanoparticles on WO_3, SnO_2, and NiO-based gas sensors", Journal of Material Chemistry A, 9, 1159–1167, 2021.

[3] W. Koo, et al., "Heterogeneous sensitization of metal-organic framework driven metal@metal oxide complex catalysts on an oxide nanofiber scaffold toward superior gas sensors", Journal of American Chemical Society, 138, 13431–13437, 2016.

[4] M. Horprathum, et al., "Ultrasensitive hydrogen sensor based on Pt-decorated WO_3 nanorods prepared by glancing-angle dc magnetron sputtering", ACS Applied Materials and Interfaces, 6, 22051–22060, 2014.

[5] O. Alev, et al., "Effect of Pt catalyst on the sensor performance of WO_3 nanoflakes towards hazardous gases", Journal of Alloys and Compounds, 32, 25376–25384, 2021.

[6] P.M. Bulemo, et al., "Controlled synthesis of electrospun hollow Pt-loaded SnO_2 microbelts for acetone sensing", Sensors and Actuators B: Chemical, 344, 130208, 2021.

[7] C. Dong, et al., "Combustion synthesis of porous Pt-functionalized SnO_2 sheets for isopropanol gas detection with a significant enhancement in response", Journal of Materials and Chemistry A, 2, 20089–20095, 2014.

[8] P.M. Bulemo, et al., "Facile Synthesis of Pt-Functionalized Meso/Macroporous SnO_2 Hollow Spheres through in Situ Templating with SiO_2 for H_2S Sensors", ACS Applied Materials and Interfaces, 10, 18183-18191, 2018.

[9] W. Guo, et al., "High-response H_2S sensor based on ZnO/SnO_2 heterogeneous nanospheres", RSC Advances, 6, 15048-15053, 2016.

[10] P.S. Kolhe, et al., "Synthesis of Ag doped SnO_2 thin films for the evaluation of H_2S gas sensing properties", Physica B, 524, 90-96, 2017.

[11] H. Zou, et al., "An Au/SnO–SnO_2 nanosheet based composite used for rapid detection of hydrogen sulfide", Analytical Methods, 15, 1315-1322, 2023.

[12] L. Liu, et al., "In Situ Growth of NiO@SnO_2 Hierarchical Nanostructures for High Performance H_2S Sensing", ACS Applied Materials and Interfaces, 11, 44829-44836, 2019.